



THE OPEN UNIVERSITY OF SRI LANKA  
B.Sc. Degree Programme / Stand alone courses 2007 / 2008  
Level 5 – Continuous Assessment Test II

CHU 3129 – INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

Duration: one and half hours

Date : 8<sup>th</sup> April, 2008

From 3.30 p.m. to 5.00 p.m.

Reg. No. ....

Question No.	Marks
1	
2	
3	
4	
Total	
Percentage	

- Answer all questions.
- Write down the answers in the spaces provided in the paper itself. Attached sheets will not be graded.
- Faraday's constant (F) = 96485 Cmol<sup>-1</sup>
- Gas constant (R) = 8.314 JK<sup>-1</sup>mol<sup>-1</sup>

1. A galvanic cell is constructed from two redox electrodes, titanium (IV) / titanium (III) and cerium (IV) / cerium (III). Assume that all the ions are at unit activity and  $E^\circ(\text{Ti}^{4+}/\text{Ti}^{3+}) = -0.04\text{V}$  and  $E^\circ(\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.61\text{V}$ .

(i) Which electrode will be the positive electrode ?

.....

(ii) Write the cell linear format (*i.e.* short hand description).

(iii) Write down the cell reactions separately for the left hand and right hand electrodes.

.....

.....

(iv) Calculate the free energy change for the spontaneous cell reaction.

(v) Deduce the change in the electro motive force (emf) of the cell (at 298 K) if the concentrations of the titanium (III) and cerium (IV) is decreased by 10 fold.

(30 marks)

2. (i) Explain the following terms in brief.

(a) Half wave potential

.....  
.....  
.....  
.....

(b) Electrode polarization

.....  
.....  
.....  
.....

- (ii) Sketch the amperometric titration curves corresponding to the situation where only the analyte in the flask is reduced.

.....

- (iii) Write down the major difference in principle of the following pairs

(a) An electrolysis cell and an electro chemical cell

.....  
.....  
.....  
.....  
.....  
.....

(b) Membrane electrode and metallic electrode

.....  
.....  
.....  
.....  
.....  
.....

- (iv) An electric current was passed through a solution of  $\text{AgNO}_3$ . After five minutes, 1.000g of Ag was deposited from the solution. Calculate the current passed ( $\text{Ag} = 107.9$ ).

(30 marks)

3. Comment briefly on the following statements.

(i) Gel permeation chromatography is different to all the other chromatographic techniques.

.....  
.....  
.....  
.....

(ii) If a mixture of  $F^-$ ,  $Cl^-$ ,  $Ar^-$  and  $I^-$  was passed through a strong anion exchange column,  $F^-$  will be eluted first.

.....  
.....  
.....

(iii) Electrophoresis cannot be considered as a chromatographic technique.

.....  
.....

(iv) In the reverse phase chromatography, the most polar compound is eluted first.

.....  
.....  
.....  
.....

(v) When the diffusion coefficient of a compound in the mobile phase ( $D_M$ ) increases, the efficiency of separation in a chromatographic column decreases.

.....  
.....  
.....  
.....  
.....  
.....  
.....  
.....

(25 marks)

4. The compound A was detected using gas chromatography with a 50 cm column in which the  $V_s$  was  $20.0 \text{ cm}^3$  and  $V_m$  was  $55.0 \text{ cm}^3$ . The retention time of A was 10.0

minutes when Air was used as the carrier gas. The retention time of air was 2.0 minutes.

(i) Calculate the retention factor for A.

(ii) Calculate the distribution coefficient of A.

(iii) The compound B showed a retention time of 10.3 minutes when the same column was used with the same conditions. Is it possible to separate A from B with a high accuracy? Explain your answer with suitable calculations.

(15 marks)



THE OPEN UNIVERSITY OF SRI LANKA

B.Sc degree programme / Stand Alone courses 2007/2008

CHU 3129 INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

Answer guide to Assignment test II

- (1) (i)  $\text{Ce}^{4+} / \text{Ce}^{3+}$   
 (ii)  $\text{Pt} / \text{Ti}^{4+}_{(a=1)}, \text{Ti}^{3+}_{(a=1)} // \text{Ce}^{4+}_{(a=1)}, \text{Ce}^{3+}_{(a=1)} / \text{Pt}$   
 (iii) LHE -  $\text{Ti}^{3+} \longrightarrow \text{Ti}^{4+} + e$   
 RHE -  $\text{Ce}^{4+} + e \longrightarrow \text{Ce}^{3+}$

(iv) 
$$E_{\text{cell}}^0 = E_R^0 - E_L^0$$

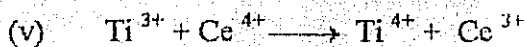
$$= 1.61 - (-0.04)$$

$$= 1.65 \text{ V}$$

$$\Delta G = -nF E_{\text{cell}}^0$$

$$= -1 \times 96485 \text{ C mol}^{-1} \times 1.65 \text{ V}$$

$$= -159200 \text{ J} = -159.2 \text{ KJ}$$



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{[\text{Ti}^{4+}][\text{Ce}^{3+}]}{[\text{Ti}^{3+}][\text{Ce}^{4+}]}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303RT}{nF} \log \frac{[\text{Ti}^{4+}][\text{Ce}^{3+}]}{[\text{Ti}^{3+}][\text{Ce}^{4+}]}$$

If  $[\text{Ti}^{3+}] = c$  and  $[\text{Ce}^{4+}] = c$ ,

$$E_{\text{cell}} = E_{\text{cell}}^0 - 0.0592 \log \frac{[\text{Ti}^{4+}][\text{Ce}^{3+}]}{(c)(c)}$$

When  $[\text{Ti}^{3+}] = 0.1c$  and  $[\text{Ce}^{4+}] = 0.1c$ ,

$$E_{0.1 \text{ cell}} = E_{\text{cell}}^0 - 0.0592 \log \frac{[\text{Ti}^{4+}][\text{Ce}^{3+}]}{(0.1c)(0.1c)}$$

$$\Delta E = E_{\text{cell}} - E_{0.1 \text{ cell}}$$

$$\Delta E = -0.0592 \log (0.01)$$

$$= 0.0592 \log \frac{1}{0.01} = 0.0592 \log 100 = 0.1184 \text{ V} = 118.4 \text{ mV}$$

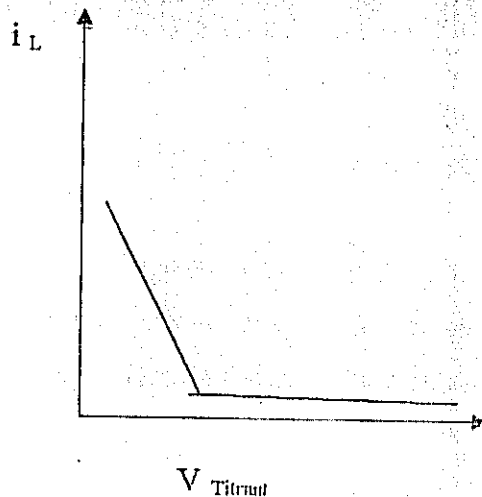
(2) (i) (a) Half wave potential

The potential at which the current is equal to half of the limiting current. It is characteristic for a given analyte.

(b) Electrode polarization

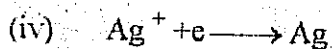
When the external voltage of an electrode is increased, the charge on it increases without increasing the current. Then the electrode is said to be polarized.

(ii)



(iii) (a) In an electrochemical cell the energy source is the spontaneous chemical reaction occurring in the cell. In an electrolysis cell the source is an externally applied voltage which imposes a chemical reaction in the cell.

(b) In metallic electrodes the electrode potential depends on the activity (concentration) of the analyte which is subjected to either oxidation or reduction. In membrane electrode it is the overall cell potential (junction potential) which is measured and analyte is not subjected to either oxidation or reduction.



$$\text{No. of moles of Ag deposited} = \frac{1.000 \text{ g}}{107}$$

$$\text{No. of moles of Ag deposited} = \frac{Q}{nF} = \frac{it}{nF} = \frac{1.000g}{107g}$$

$$i = \frac{1.000g}{107g} \times \frac{1 \times 96485 C mol^{-1}}{5 \times 60s} = 3.00A$$

- (3) (i) In gel permeation chromatography the separation is based on the size differences and not by the differences of strength of the intermolecular forces between the stationary phase and the compounds.
- (ii) The affinity of an ion for the resin depends on the charge of the ion and the size of the hydrated ion. Size of the hydrated ion  $\propto \frac{1}{\text{affinity}}$

The smallest ion is having the largest size when hydrated thus having the lowest affinity.

- (iii) There is no mobile phase in electrophoresis.
- (iv) In reverse phase chromatography, the stationary phase is non polar and mobile phase is polar. Therefore, polar compounds are less retained.
- (v)  $B \propto D_M$  or  $B = 2YD_M$

$$H = A + \frac{B}{U} + CU, \quad B \propto H$$

Therefore, Height equivalent to theoretical plate (H) increases as  $D_m$  increases thus reducing the column efficiency.

(4) (i) Retention factor,  $K'_A = \frac{t_A - t_M}{t_M} = \frac{10 - 2}{2} = 4$

(ii)  $K'_A = \frac{K_A V_S}{V_M}$        $K_A = \frac{V_M K'_A}{V_S} = \frac{55 \times 4}{20} = 11$

(iii) No.

$$t_B = 10.3 \text{ min}$$

$$\text{Selectivity factor } (\alpha) = \frac{t_B - t_M}{t_A - t_M} = \frac{10.3 - 2}{10 - 2} = \frac{8.3}{8} = 1.0375$$

Selectivity factor is closer to 1 thus the separation is poor.

